Solvent Dependence of the Optical Rotatory Dispersion Spectra of Some 17-Phenylazo-steroids

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As part of our studies on the optical rotatory dispersion spectra of the phenylazo-chromophore[1] we have extended our work to a variety of phenylazo-steroids. This Communication concerns compounds (II—VII) having this functional group at C-17.

Compounds (II) and (III) were first prepared from dehydroepiandrosterone phenylhydrazone (I) by Chaplin, Hey, and Honeyman,[2] but the configuration of (II) at C-17 was not determined by these workers. We have converted (II), by catalytic reduction, followed by acetylation, into 17β-acetamido-5α-androstan-3β-yl acetate,[3] proving that (II) has the 17β-configuration, and have assigned the same configuration to the phenylazo-group in (III) since attack by oxygen on the phenylhydrazone (I) will occur from the α-face of the molecule. In pyridine or dioxan solutions, compounds (II) and (III) both showed negative Cotton effects associated with the n–π^* transition of the phenylazo-group around 400 mμ. In carbon tetrachloride, benzene, or chloroform solution the o.r.d. spectrum of (II) remained virtually unaltered whilst that of (III) underwent a striking change, the negative curve ($[\Phi] \sim 7000°$) being replaced by a positive curve of about the same amplitude.

This phenomenon we ascribe to the transition from an intermolecularly hydrogen-bonded form (VIII) in pyridine or dioxan in which the hydroperoxy-group is bonded to the solvent, to an intramolecularly hydrogen-bonded form (IX) in which the phenylazo-group is rotated to a new, fixed position.

The o.r.d. spectrum of compound (III) in mixed solvents is of interest. In carbon tetrachloride–dioxan mixtures a transition from negative to positive curves takes place (Figure), all of the curves[†] passing through one point for which we propose the name "*isorotatic point,*" by analogy

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[†] Curves were also obtained for mixtures containing 30 and 10% of carbon tetrachloride: both fell between the 0 and 60% curves on the Figure and passed through the isorotatic point.

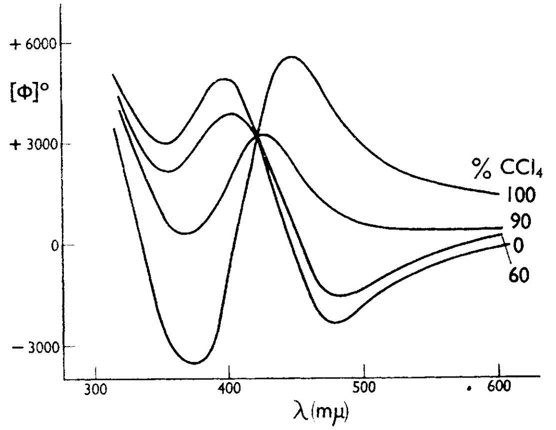
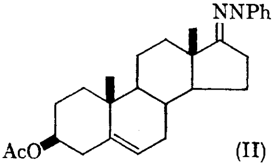


FIGURE. *O.r.d. spectra of compound* (III) *in dioxan–carbon tetrachloride mixtures.*

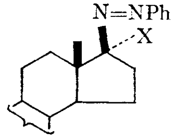
with isosbestic points in absorption spectra. As with isosbestic points,[4] the presence of an isorotatic point does not prove the presence of only two species in solution [*i.e.*, (VIII) and (IX)], though it strongly suggests that this is so.

We have also prepared the substituted 17-phenylazo-steroid derivatives (IV)—(VII) by standard procedures from the phenylhydrazone (I). Like compound (II) these showed negative Cotton effects in all the above solvents and we have assigned the 17β-configuration to the phenylazo-group in these compounds because of this and because of their mode of formation.

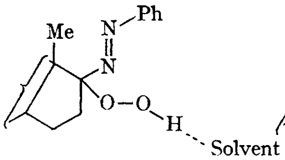
It seems likely that equilibria of this type probably play a part in causing the complex variations in the o.r.d. spectra of phenylazo-sugars,[1] for which similar isorotatic points have been observed.[5]



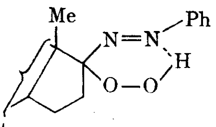
(I)



(II) X=H; (III) X=OOH;
(IV) X=OAc; (V) X=OEt;
(IV) X=OMe; (VII) X=OCO·Ph



(VIII)



(IX)

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[2] A. F. Chaplin, D. H. Hey, and J. Honeyman, *J. Chem. Soc.*, 1959, 3194.

[3] J. Schmidt-Thome, *Chem. Ber.*, 1955, **88**, 895.

[4] M. D. Cohen and E. Fischer, *J. Chem. Soc.*, 1962, 3044.

[5] E. O. Bishop, R. D. Guthrie, and J. E. Lewis, unpublished work.